Errors in Measuring the Wave-Height of Polarogram. I. Mathematical Discussion

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(Received June 16, 1954)

Introduction

In the polarographic quantitative analysis, we may know the amount of material by measuring the wave-height which is obtained after the graphical construction on a polarogram. Therefore it is one of the necessary conditions in the precise polarographic determination, that the polarogram is so taken that the errors of the graphical construction become the least possible.

According to Kolthoff and Lingane[1], any tendency of the limiting current to change with changing applied e.m.f. is greatly magnified by the magnification of a wave and so when the wave is not well-developed, mere magnification of a wave does not necessarily increase the accuracy with which it can be measured. This discussion may hold rather in precision than in accuracy where the so-called errors are related to reliability, precision and accuracy[2]. Therefore a degree of magnification of a wave should be selected in the precise polarographic analysis. In this paper this degree of magnification is discussed mathematically.

Mathematical Calculation of Errors

In order to measure the wave-height of the polarogram *ACB* (Fig. 1), we may use various methods of graphical construction. This discussion holds when the line intersection method[3] treats curves. That is, tangents ξ and η are drawn through the mid-points of straight parts or inflexion-points *A* and *B*, respectively, just before and just after the wave, and a third tangent is drawn through the inflexion-point C of wave. The vertical distance between the two intersection *X* and *Y* thus obtained corresponds to the wave-height *h*.

Now, when the voltage axis represents abscissa and the current axis ordinate, writing coordinates of A, B, C, *X* ane *Y*, as (a_1, b_1), (a_2, b_2), (a_3, b_3), $(x_1, y_1)$and (x_2, y_2), respectively and putting angles at which ξ, η, and ζ intersect the abscissa, φ, ψ and θ, respectively, we have

$$h=f\ (a_1,\ b_1,\ a_2,\ b_2,\ a_3,\ b_3,\ \theta,\ \varphi,\ \psi). \qquad (1)$$

But three respective variables in bracket of (a_1, d_1, φ), (a_2, b_2, ψ) or (a_3, b_3, θ) are not independent of one another and the relations between these variables cannot be discussed generally.

On the other hand, the first procedure of construction is to determine (a_1, b_1) etc. and the next is to determine φ etc. And, for instance, on determining (a_1, b_1), b_1 will be

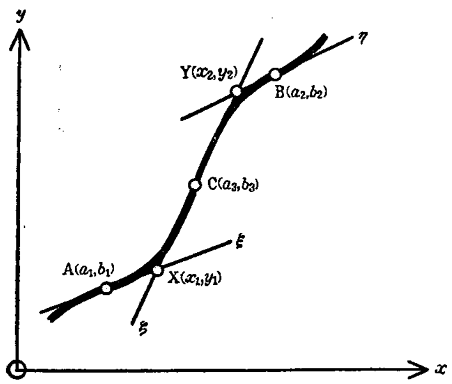

Fig. 1.

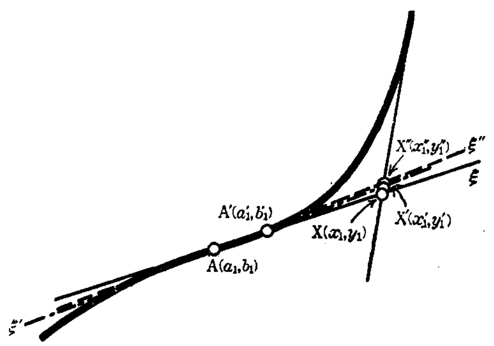

Fig. 2.

1) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed. p. 328 (1952) Interscience Publishers, New York.

2) K. Ishikawa, *Kagaku-no-Ryoiki*, extra-ed. 10. ("Statistics for Chemists") p. 26 (1953).

3) D. F. Boltz, "Selected Topics in Modern Instrumental Analysis," p. 41 (1952) Prentice- Hall, Inc., New York.

determined after a_1 is fixed. Perhaps the error, which occurs in the determination of b_1, may be negligibly small, if a_1 is fixed. So assuming that b_1 responds strictly to a_1, we have

$$h=f\ (a_1,\ a_2,\ a_3,\ \theta,\ \varphi,\ \psi) \tag{2}$$

Nevertheless another assumption is needed, as two respective variables in a bracket of $(a_1,\ \varphi)$, $(a_2,\ \psi)$ or $(a_3,\ \theta)$ are not independent of each other.

That is, if a point $(a_1',\ b_1')$ is found instead of the actual point $(a_1,\ b_1)$ and a tangent ξ' is erected instead of the actual tangent ξ let us draw through the point $(a_1,\ b_1)$ a line ξ'' in parallel with ξ' (Fig. 2). The difference between the wave-height with ξ' and the one with ξ'' $(|y_1''-y_1'|)$ shall be assumed as negligibly small in comparison with the difference between the wave-height with ξ and the one with ξ' $(|y_1'-y_1|)$. And the corresponding assumptions of $(a_2,\ \psi)$ and $(a_3,\ \theta)$ shall be considered. With these assumptions the errors in determination of φ, ψ and θ contain those in determination of a_1, a_2 and a_3. Thus writing

$$h=f\ (\theta,\ \varphi,\ \psi) \tag{3}$$

we may calculate the amount of error of h.

Then, by transferring the origin to C in Fig. 1 and displacing the axes parallelly, the following equations can be obtained.

$$\left.\begin{aligned} \frac{b_1^0-y_1^0}{a_1^0-x_1^0}&=\tan\varphi=m\\ \frac{b_2^0-y_2^0}{a_2^0-x_2^0}&=\tan\psi=n\\ \frac{y_1^0}{x_1^0}=\frac{y_2^0}{x_2^0}&=\tan\theta=l \end{aligned}\right\} \tag{4}$$

Where $(a_1^0,\ b_1^0)$, $(a_2^0,\ b_2^0)$, $(0,\ 0)$, $(x_1^0,\ y_1^0)$ and $(x_2^0,\ y_2^0)$ are the coordinates of A, B, C, X and Y, respectively.

Hence we have

$$\left.\begin{aligned} y_1^0&=\frac{(b_1^0-a_1^0m)l}{l-m}\\ y_2^0&=\frac{(b_2^0-a_2^0n)l}{l-n} \end{aligned}\right\} \tag{5}$$

$$h=y_2^0-y_1^0=\frac{(b_2^0-a_2^0n)l}{l-n}-\frac{(b_1^0-a_1^0m)l}{l-m} \tag{6}$$

Now, assuming that the probability density functions of h, θ, φ and ψ are all symmetrical, we have from the familiar formula of error transmission[4]:

$$e_h^2=\left(\frac{\partial h}{\partial\theta}\right)^2e_\theta^2+\left(\frac{\partial h}{\partial\varphi}\right)^2e_\varphi^2+\left(\frac{\partial h}{\partial\psi}\right)^2e_\psi^2 \tag{7}$$

4) S. Miyamoto, "Theory and Calculation of Error," p. 81 (1951) Kosei-sha, Tokyo.

where e_h^2 etc. are the mean squares of errors of h etc., respectively. And from Eq. (6), it follows that

$$\left.\begin{aligned} \frac{\partial h}{\partial\varphi}&=\frac{(a_1^0l-b_1^0)l}{(l-m)^2}(1+m^2)\\ \frac{\partial h}{\partial\psi}&=\frac{-(a_2^0l-b_2^0)l}{(l-n)^2}(1+n^2)\\ \frac{\partial h}{\partial\theta}&=-\left\{\frac{(b_2^0-a_2^0n)n}{(l-n)^2}-\frac{(b_1^0-a_1^0m)m}{(l-m)^2}\right\}(1+l^2) \end{aligned}\right\} \tag{8}$$

Also the relative errors of h are more important than the absolute errors shown in Eq. (7), since the comparative method is usually used in the polarographic quantitative analysis. From Eq. (7) the relative errors are given by,

$$\left(\frac{e_h}{h}\right)^2=\frac{1}{h^2}\left(\frac{\partial h}{\partial\theta}\right)^2e_\theta^2+\frac{1}{h^2}\left(\frac{\partial h}{\partial\varphi}\right)^2e_\varphi^2+\frac{1}{h^2}\left(\frac{\partial h}{\partial\psi}\right)^2e_\psi^2 \tag{9}$$

The Variation of Magnitude of Error with Span Voltage and Sensitivity

When a polarogram is taken with span voltage p times as high and sensitivity q times as high as those with which the original polarogram in Fig. 1 is taken, the new polarogram will be transformed into one of dimensions one pth times in abscissa and q times in ordinate as great as the original. Let us compare the errors of construction on those polarograms as follows.

That is, if the transformation is performed without transferring the point C, the coordinates of A and B will be $(a_1^0/p_1,\ qb_1^0)$ and $(a_2^0/p,\ qb_2^0)$ respectively. Thus

$$\left.\begin{aligned} \tan\varphi_{pq}&=pqm\\ \tan\psi_{pq}&=pqn\\ \tan\theta_{pq}&=pql \end{aligned}\right\} \tag{10}$$

where φ_{pq}, ψ_{pq} and θ_{pq} are angles at which after the transformation tangents ξ, η and ζ intersect abscissa respectively.

Hence from Eq. (8) we have

$$\begin{aligned} \frac{\partial h_{pq}}{\partial\varphi_{pq}}&=\frac{(a_1^0l-b_1^0)l}{(l-m)^2}\cdot\frac{1+p^2q^2m^2}{p}\\ &=\left(\frac{\partial h}{\partial\varphi}\right)\frac{1+p^2q^2m^2}{p(1+m^2)}\\ \frac{\partial h_{pq}}{\partial\psi_{pq}}&=\frac{-(a_2^0l-b_2^0)l}{(l-n)^2}\cdot\frac{1+p^2q^2n^2}{p}\\ &=\left(\frac{\partial h}{\partial\psi}\right)\frac{1+p^2q^2n^2}{p(1+n^2)} \end{aligned}$$

$$\left.\begin{aligned}\frac{\partial h_{pq}}{\partial\theta_{pq}}&=-\left\{\frac{(b_2{}^0-a_2{}^0n)n}{(l-n)^2}-\frac{(b_1{}^0-a_1{}^0m)m}{(l-m)^2}\right\}\frac{1+p^2q^2l^2}{p(1+l^2)}\\&=\left(\frac{\partial h}{\partial\theta}\right)\frac{1+p^2q^2l^2}{p(1+l^2)}\end{aligned}\right\}\quad(11)$$

And in such a transformation the wave-height varies also. writing the wave-height after the transformation as h_{pq}, it follows that

$$h_{pq}=qh \quad (12)$$

Furthermore, the magnitude of e_θ, e_φ and e_ϕ may vary. Now we assume on these variations as follows.

(1) If the curvature on A, B or C of the polarogram in Fig. 1 are greater, or the curve near such a point is linear over a wider range, the amount of e_θ, e_φ or e_ϕ will not vary with the transformation.

(2) If the curve near such a point is linear but the linear portion is shorter, the amount of e_θ, e_φ or e_ϕ will be inversely proportional to the length of this linear portion.

With the assumption (1), for instance, it is seen that

$$\frac{1}{h_{pq}{}^2}\left(\frac{\partial h_{pq}}{\partial\theta_{pq}}\right)^2 e_{\theta pq}{}^2=\frac{1}{h^2}\left(\frac{\partial h}{\partial\theta}\right)^2 e_\theta{}^2\frac{(1+p^2q^2l^2)^2}{p^2q^2(1+l^2)^2} \quad (13)$$

And by partially differentiating Eq. (13) with respect to p or q, we have

$$\frac{\partial}{\partial p}\left\{\frac{1}{h^2_{pq}}\left(\frac{\partial h_{pq}}{\partial\theta_{pq}}\right)^2 e_{\theta pq}{}^2\right\}=\frac{1}{h^2}\left(\frac{\partial h}{\partial\theta}\right)^2 e_\theta{}^2\frac{2(1+p^2q^2l^2)(p^2q^2l^2-1)}{p^3q^2(1+l^2)^2}$$

$$\frac{\partial}{\partial q}\left\{\frac{1}{h_{pq}{}^2}\left(\frac{\partial h_{pq}}{\partial\theta_{pq}}\right)^2 e_{\theta pq}{}^2\right\}=\frac{1}{h^2}\left(\frac{\partial h}{\partial\theta}\right)^2 e_\theta{}^2\frac{2(1+p^2q^2l^2)(p^2q^2l^2-1)}{p^2q^3(1+l^2)^2}$$

Hence when $pql=1$ ($l\neq0$), Eq. (13) takes the minimum value. As for

$$\frac{1}{h^2_{pq}}\left(\frac{\partial h_{pq}}{\partial\varphi_{qp}}\right)^2 e^2_{\varphi pq} \text{ or } \frac{1}{h^2_{pq}}\left(\frac{\partial h_{pq}}{\partial\psi_{pq}}\right)^2 e_{\phi pq}{}^2$$

it takes the minimum value also, when $pqm=1$ or $pqn=1$, respectively. But if $l=0$, $m=0$ or $n=0$, it takes the smaller value, with the increase of p and q.

Next, with the assumption (2), for instance, it is seen that

$$\frac{1}{h_{pq}{}^2}\left(\frac{\partial h_{pq}}{\partial\theta_{pq}}\right)^2 e_{\theta pq}{}^2=\frac{1}{h^2}\left(\frac{\partial h}{\partial\theta}\right)^2 e_\theta{}^2\frac{1+p^2q^2l^2}{q^2(1+l^2)} \quad (14)$$

where

$$e_{\theta pq}{}^2=e_\theta{}^2\frac{p^2(1+l^2)}{1+p^2q^2l^2} \quad (15)$$

and

$$\frac{\partial}{\partial p}\left\{\frac{1}{h^2_{pq}}\left(\frac{\partial h_{pq}}{\partial\theta_{pq}}\right)^2 e_{\theta pq}{}^2\right\}=\frac{1}{h^2}\left(\frac{\partial h}{\partial\theta}\right)^2 e_\theta{}^2\frac{1+2pq^2m^2}{q^2(1+m^2)}>0 \quad (16)$$

$$\frac{\partial}{\partial q}\left\{\frac{1}{h_{pq}{}^2}\left(\frac{\partial h_{pq}}{\partial\theta_{pq}}\right)^2 e_{\theta pq}{}^2\right\}=\frac{1}{h^2}\left(\frac{\partial h}{\partial\theta}\right)^2 e_\theta{}^2\left\{\frac{-2}{q^3(1+m^2)^2}\right\}<0 \quad (17)$$

Hence, Eq. (14) takes the greater value with increasing p and Eq. (14) takes the smaller value with increasing of q.

As for

$$\frac{1}{h_{pq}{}^2}\left(\frac{\partial h_{pq}}{\partial\varphi_{pq}}\right)^2 e^2_{\varphi pq} \text{ or } \frac{1}{h_{pq}{}^2}\left(\frac{\partial h_{pq}}{\partial\psi_{pq}}\right)^2 e^2_{\phi pq},$$

the same relationships hold.

Discussion

From the above mathematical calculation, the relative error of h should be minimum when $pql=1$ or $\theta_{pq}=45°$, if the error in construction of the tangent through C in Fig. 1 is more pronounced than other errors and its magnitude varies after the manner shown by the assumption (1). And if the errors in construction of the tangents through B and C are both pronounced and their magnitudes vary after the manner shown by the assumption (1), $1/m>pq>1/l$, where $l>m$ or $\theta_{pq}>45°>\varphi_{pq}$, is the necessary condition for the minimum value of the relative error of h.

On the other hand, when in all the errors the assumption (2) holds, the relative error of h becomes smaller, with decreasing p and increasing q.

But we must remember the fact that the manner of variation of error of θ_{pq} etc. can also change with the transformation of the curve.

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